Measurement of Circular Dichroism in the Ultra-Violet Regions. I.

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Introduction. A method of measuring circular dichroism in the ultraviolet as well as the visible regions was devised by Kuhn and Braun.⁽¹⁾ The general principle of the method is as follows. By means of a half-shadow polarizer of a split prism and a Fresnel rhomb set parallel to the polarizer, two elliptically polarized rays of opposite sign and of equal ellipticity are produced. On traversing d cm. of a c mol/l. solution of an optically active compound whose molar extinction coefficients for left and right circular vibrations are ε_l and ε_r, the two rays will have their ellipticities changed. By rotating the polarizer, the ellipticities of the rays incident on the solution can be made unequal until those of the emergent rays are again equal. This is tested by an analyser placed so as to transmit only those vibrations corresponding to the minor axes of the two ellipses. Let τ be the angle through which the polarizer has been rotated to obtain an equal brightness after passing through the optical system, then the difference between the molar extinction coefficients is given by the following relation

$$\varepsilon_l-\varepsilon_r=\frac{4\tau}{cd}\,. \qquad (1)$$

In deriving the relation, however, the following limitations have been introduced. Let θ be half the angle between the two vibration directions of the polarizer. The values of θ and τ should be so small as to satisfy the relations, $\tan\theta\simeq\theta$, $\tan(\theta+\tau)\simeq\theta+\tau$ and $\tan(\theta-\tau)\simeq\theta-\tau$, and α, the rotation caused by the active compound, should also be very small. Besides these limitations, some more approximate calculations have been introduced in course of derivation of the relation (1), and consequently it seems insufficient for further discussions. The present author has derived a general equation for circular dichroism measurements in which both the polarizer and the analyser are rotated and all

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(1) Kuhn and Braun, *Z. physik. Chem.*, B, **8** (1930), 445.

the above-mentioned limitations have been abolished. By means of the equation, experimental conditions have been discussed.

Derivation of the Equation. Let 2θ be the angle between the vibration directions of prisms P_1 and P_2 of the half-shadow polarizer and τ, the angle between the bisectrix of the two planes of vibration of P and the Fresnel rhomb F, whose vibration directions are taken as co-ordinate axes throughout the calculation. Then the plane polarized rays produced by the prisms P_1 and P_2 contain $\tau+\theta$ and $\tau-\theta$ respectively with the x-axis. The intensity of the two rays after passing through the polarizer being equal, the amplitude is denoted by a_0. Then the two rays may be expressed by

$$a = a_0 \cos 2\pi\nu t \, .$$

On entering the Fresnel rhomb each of these rays is split into two components, one propagating in a plane parallel to the rhomb and the other perpendicular. The amplitudes of these components, a_x and a_y, are

$$\left.\begin{aligned}(a_x)_1 &= a_0 \,|\cos(\tau+\theta)| \\ (a_y)_1 &= a_0 \,|\sin(\tau+\theta)|\end{aligned}\right\} \text{ for } P_1,$$

and

$$\left.\begin{aligned}(a_x)_2 &= a_0 \,|\cos(\tau-\theta)| \\ (a_y)_2 &= a_0 \,|\sin(\tau-\theta)|\end{aligned}\right\} \text{ for } P_2 .$$

The light waves before the first total reflexion in the rhomb are

$$\left.\begin{aligned}x_1 &= a_0 \cos(\tau+\theta) \cos 2\pi\nu t \\ y_1 &= a_0 \sin(\tau+\theta) \cos 2\pi\nu t\end{aligned}\right\} \text{ for } P_1,$$

and

$$\left.\begin{aligned}x_2 &= a_0 \cos(\tau-\theta) \cos 2\pi\nu t \\ y_2 &= a_0 \sin(\tau-\theta) \cos 2\pi\nu t\end{aligned}\right\} \text{ for } P_2 .$$

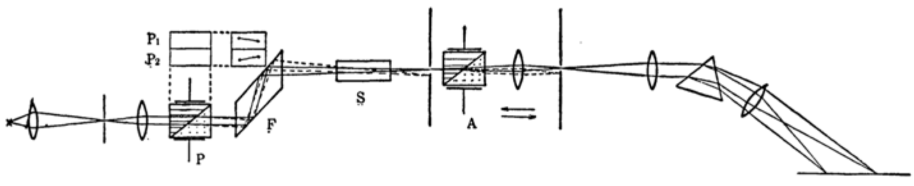

Fig. 1.

After the second total reflexion in the rhomb, each of these two pairs of plane polarized rays receives a phase difference of $\frac{\pi}{2}$, and the waves become

$$\left.\begin{aligned} x_1 &= a_0 \cos(\tau+\theta)\cos 2\pi\nu t \\ y_1 &= a_0 \sin(\tau+\theta)\sin 2\pi\nu t \end{aligned}\right\} \text{for } P_1,$$

and

$$\left.\begin{aligned} x_2 &= a_0 \cos(\tau-\theta)\cos 2\pi\nu t \\ y_2 &= a_0 \sin(\tau-\theta)\sin 2\pi\nu t \end{aligned}\right\} \text{for } P_2.$$

The resultant vibration for P_1 and P_2 after passing through the rhomb may, therefore, be expressed as

$$\left.\begin{aligned} \mathbf{R}_1 &= \mathbf{i}a_0 \cos(\tau+\theta)\cos 2\pi\nu t + \mathbf{j}a_0 \sin(\tau+\theta)\sin 2\pi\nu t \\ \text{and} \quad \mathbf{R}_2 &= \mathbf{i}a_0 \cos(\tau-\theta)\cos 2\pi\nu t + \mathbf{j}a_0 \sin(\tau-\theta)\sin 2\pi\nu t. \end{aligned}\right\} \qquad (2)$$

These expressions represent elliptically polarized lights whose sense of rotation depends on τ and θ. The elliptically polarized ray is lævorotatory when P_1 is in the first and the third quadrant, and dextrorotatory otherwise. The same holds for P_2.

First the intensity of the elliptically polarized lights is compared directly with the analyser A. Let the angle between the analyser and the Fresnel rhomb be δ_0, at which the two fields of the half-shadow are of equal brightness, then

$$a_0^2 \cos^2(\tau+\theta)\cos^2\delta_0 + a_0^2 \sin^2(\tau+\theta)\sin^2\delta_0$$
$$= a_0^2 \cos^2(\tau-\theta)\cos^2\delta_0 + a_0 \sin^2(\tau-\theta)\sin^2\delta_0.$$

Solving this equation we obtain

$$\tan\delta_0 = \pm 1. \qquad \therefore\ \delta_0 = \frac{\pi}{4}(1\pm 2n).$$

Then δ_0 is independent of τ and θ; in other words the two fields of the half-shadow are of equal brightness when the analyser is placed at $\frac{\pi}{4}$ or $\frac{3}{4}\pi$ referring to the Fresnel rhomb, whatever the angle between the polarizer and the rhomb and that between the two vibration directions of the half-shadow polarizer may be. This relation gives us the means of determining the relative angular position of the analyser referred to the Fresnel rhomb and consequently the zero point of the measurement.

Next let us consider the case when a solution of active substance is introduced between the Fresnel rhomb and the analyser. As the active substance has different extinction coefficients for left and right circularly polarized vibrations, each of the elliptically polarized rays represented by the equations (2) should first be transformed as a resultant of circularly polarized waves of opposite rotatory sense.

Thus
$$\mathbf{R}_1 = \frac{a_0}{2}\left\{\cos(\tau+\theta)+\sin(\tau+\theta)\right\}(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)$$
$$+\frac{a_0}{2}\left\{\cos(\tau+\theta)-\sin(\tau+\theta)\right\}(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t)\ ,$$

or

$$\left.\begin{aligned}
\mathbf{R}_1 &= \frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}+\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)\\
&\quad+\frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t)\,.\\
&\text{And similarly}\\
\mathbf{R}_2 &= \frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}+\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)\\
&\quad+\frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t)\,.
\end{aligned}\right\}\qquad (2)'$$

In each of these equations the first and the second term represents a circularly polarized ray whose sense of rotation is anticlockwise and clockwise respectively.

After traversing the solution S, the vibrations are changed as follows. follows.

$$\mathbf{R}_1' = \frac{a_0}{\sqrt{2}}e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)$$
$$+\frac{a_0}{\sqrt{2}}e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t)\ ,$$

or
$$\mathbf{R}_1' = \mathbf{i}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}\cos 2\pi\nu t$$

$$+\mathbf{j}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}\sin 2\pi\nu t\,. \tag{3}$$

$$\mathbf{R}_2'=\mathbf{i}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}\cos 2\pi\nu t$$

$$+\mathbf{j}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}\sin 2\pi\nu t\,. \tag{4}$$

Both the expressions (3) and (4) represent elliptically polarized rays.

The intensity of the two half-shadow fields observed through the analyser A, which is placed at an angle ω to the common axis of the elliptically polarized rays, (3) and (4), corresponding to the x-axis of the co-ordinates, is given by the following expressions.

$$I_1=\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}^2\cos^2\omega$$

$$+\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}^2\sin^2\omega$$

$$=\frac{a_0^2}{2}\left\{e^{-\varepsilon_l cd}\sin^2\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\varepsilon_r cd}\sin^2\left(\frac{\pi}{4}-\tau-\theta\right)\right.$$

$$\left.+e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2(\tau+\theta)\cos 2\omega\right\}. \tag{5}$$

$$I_2=\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}^2\cos^2\omega$$

$$+\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}^2\sin^2\omega$$

$$=\frac{a_0^2}{2}\left\{e^{-\varepsilon_l cd}\sin^2\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\varepsilon_r cd}\sin^2\left(\frac{\pi}{4}-\tau+\theta\right)\right.$$

$$\left.+e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2(\tau-\theta)\cos 2\omega\right\}. \tag{6}$$

$$\therefore\quad I_1-I_2=\frac{a_0^2}{2}\sin 2\theta\Big\{\Big(e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}\Big)\cos 2\tau-2e^{-(\varepsilon_l+\varepsilon_r)cd}\sin 2\tau\cos 2\omega\Big) \tag{7}$$

and
$$I_1+I_2=\frac{a_0^2}{2}\Big\{e^{-\varepsilon_l cd}+e^{-\varepsilon_r cd}+\left(e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}\right)\cos 2\theta\sin 2\tau+2e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2\theta\cos 2\tau\cos 2\omega\Big\}\,. \tag{8}$$

When the two half-shadow fields are of equal brightness, the expression (7) must be zero. As $\sin 2\theta$ can not be zero, we obtain

$$e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}=2e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\tan 2\tau\cos 2\omega\,. \tag{9}$$

$$\therefore\quad e^{\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd}-e^{-\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd}=2\tan 2\tau\cos 2\omega\,,$$

or
$$\sinh\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd=\tan 2\tau\cos 2\,\omega\,. \tag{9$'$}$$

$$\therefore\quad \varepsilon_r-\varepsilon_l=\frac{2}{cd}\operatorname{arcsinh}(\tan 2\tau\cos 2\omega)\,. \tag{10}$$

Now τ is the angle between the polarizer and the Fresnel rhomb, and ω is given by $\omega=\delta-\alpha$, where δ is the angle between the Fresnel rhomb and the analyser and α is the angle of rotation. By measuring these angles, the circular dichroism can be calculated by the relation (10).

Approximate Equations. As we have introduced neither limitation nor approximation of any kind in course of calculation, the relation (10) holds for any values of θ, ω, and τ, as well as for any values of c and d, provided that the two fields observed through the analyser are of equal brightness.

In special cases when $\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd$ is small,

$$\varepsilon_e-\varepsilon_l\simeq\frac{2}{cd}\tan 2\tau\cos 2\omega\,. \tag{11}$$

Moreover, when ω is $\frac{\pi}{2}$ and τ is very small, we obtain an approximate equation,

$$\varepsilon_l-\varepsilon_r\simeq\frac{4\tau}{cd} \tag{1}$$

which is identical with that of Kuhn and Braun referred to in the introduction. In other words the Kuhn's equation is one of the most special cases of our equation (10).

Calculation of the error caused by applying the approximate equation (1) is complicated and very difficult, as there are too many approximations and neglections as to τ and $(\varepsilon_r-\varepsilon_l)cd$ as well as α which is again a function of c and d. Consequently it is impossible to find the range of applicability of the approximate equation (1).

On the other hand, however, it may be easily determined for the approximate equation (11) how far it could be applied without causing serious error in the results of the measurement. The calculation is as follows. From the relation (10)

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l}=-\frac{\mathrm{d}c}{c}-\frac{\mathrm{d}d}{d}+\frac{\mathrm{d}(\tan 2\tau\cos 2\omega)}{\sqrt{1+\tan^2 2\tau\cos^2 2\omega}\ \mathrm{arcsinh}\,(\tan 2\tau\cos 2\omega)}\,. \tag{12}$$

$$\mathrm{arcsinh}\,(\tan 2\tau\cos 2\omega)=\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd\equiv x\quad(\text{put}). \tag*{(10)$'$}$$

Then

$$\tan 2\tau\cos 2\omega=\sinh x=x+\frac{x^3}{3!}+\frac{x^5}{5!}+\frac{x^7}{7!}+\cdots\,. \tag*{(9)$''$}$$

Now the approximate equation (11) may be rewritten as

$$\tan 2\tau\cos 2\omega\simeq x. \tag*{(11)$'$}$$

Thus the error caused by using the approximate equation (11) is given by comparing (9)″ and (11)′

$$\mathrm{d}(\tan 2\tau\cos 2\omega)=-\left\{\frac{x^3}{3!}+\frac{x^5}{5!}+\cdots\right\}. \tag{13}$$

Substituing (9)″ and (13) in (12), we obtain

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l}=-\frac{\mathrm{d}c}{c}-\frac{\mathrm{d}d}{d}-\frac{\dfrac{x^2}{3!}+\dfrac{x^4}{5!}+\cdots}{\sqrt{1+\tan^2 2\tau\cos^2 2\omega}}\,.$$

As the first and the second term has nothing to do with the approximate equation,

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l}=-\frac{\dfrac{x^2}{3!}+\dfrac{x^4}{5!}+\cdots}{\sqrt{1+\tan^2 2\tau\cos^2 2\omega}}\,. \tag*{(12)$'$}$$

Therefore the value of x which would provoke an error of 1% in $(\varepsilon_r - \varepsilon_l)$ may be computed as follows.

$$-\frac{1}{100} = -\frac{\dfrac{x^2}{3!} + \dfrac{x^4}{5!} + \cdots}{\sqrt{1+\tan^2 2\tau \cos^2 2\omega}} .$$

When x is a small fraction

$$\frac{x^4}{5!} + \frac{x^2}{3!} = \frac{1}{100}\sqrt{1+x^2} .$$

Solving the equation, we obtain

$$x = \pm 0.253.$$

In order to make use of the approximate equation (11') with a permissible error less than 1%, the following condition should be complied with.

$$|(\varepsilon_r - \varepsilon_l)|\, cd < 0.50.$$

Similarly for a permissible error less than 0.1

$$|(\varepsilon_r - \varepsilon_l)|\, cd < 0.15.$$

and for 0.01

$$|(\varepsilon_r - \varepsilon_l)|\, cd < 0.04.$$

Circular Dichroism of Ammonium α-Bromocamphor-π-Sulphonate. The molar extinction coefficient κ (as in $I = I_0 \times 10^{\kappa c d}$) and the specific rotation $[\alpha]$ of the salt were measured with 0.01 mol/l. aqueous solutions with thicknesses between 0.3 and 4 cm. The circular dichroism $\kappa_r - \kappa_l$, i.e., $0.434 \times (\varepsilon_r - \varepsilon_l)$ was determined according to the method described above. The strength of the solution was 0.01 mol/l. and the thickness of the layer was 1 cm. throughout the measurements. The results are shown in Fig. 2.

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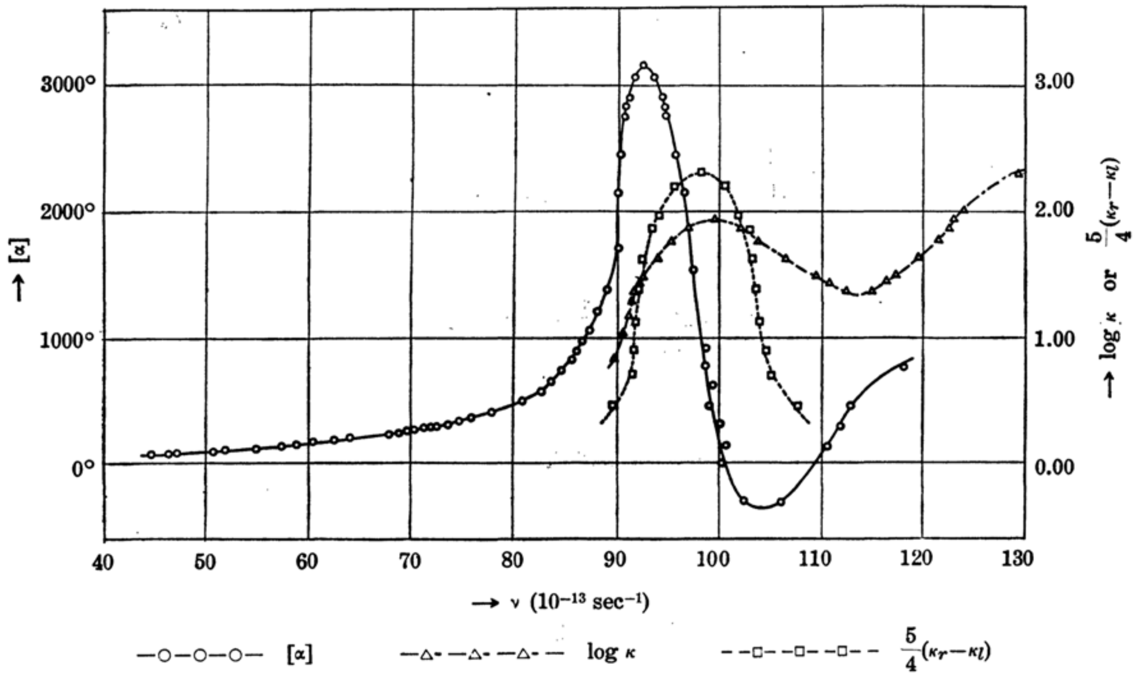

Fig. 2.

Summary.

1. An accurate method of measuring circular dichroism has been proposed.

2. The general equation for the measurement has been worked out.

$$\varepsilon_r-\varepsilon_l=\frac{2}{cd}\,\text{arcsinh}\,(\tan 2\tau \cos 2\omega)\ .$$

3. The range of applicability was discussed for the approximate equation,

$$\varepsilon_r-\varepsilon_l=\frac{2}{cd}\tan 2\tau \cos 2\omega\ .$$

In order to make use of this equation with permissible errors less than 0.01, 0.1, and 1%, the following conditions should be complied with:

$$|(\varepsilon_r-\varepsilon_l)cd| < 0.04 \qquad \text{for} \quad 0.01\%\ ,$$

$$|(\varepsilon_r - \varepsilon_l)cd| < 0.15 \quad \text{for} \quad 0.1\ \% ,$$

and

$$|(\varepsilon_r - \varepsilon_l)cd| < 0.50 \quad \text{for} \quad 1\ \% .$$

4. The light absorption, the rotatory dispersion, and the circular dichroism in the visible and the ultra-violet regions were measured for ammonium α-bromocamphor-π-sulphonate.

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